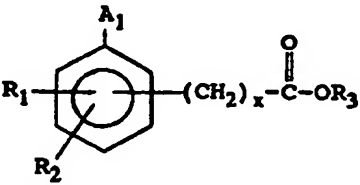


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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US94/13797 (22) International Filing Date: 2 December 1994 (02.12.94) (30) Priority Data: 08/162,416                      3 December 1993 (03.12.93)    US (71) Applicant: CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US). (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
(54) Title: POLYALKYL NITRO AND AMINO AROMATIC ESTERS AND FUEL COMPOSITIONS CONTAINING THE SAME		
(57) Abstract <p>Polyalkyl nitro and amino aromatic esters having formula (I): wherein A<sub>1</sub> is nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms; R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R<sub>3</sub> is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and x is an integer from 0 to 10. The polyalkyl nitro and amino aromatic esters of formula (I) are useful as fuel additives for the prevention and control of engine deposits.</p> <div style="text-align: center;">  <p style="text-align: right;">(I)</p> </div>		

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01 POLYALKYL NITRO AND AMINO AROMATIC ESTERS  
02 AND FUEL COMPOSITIONS CONTAINING THE SAME  
03

04 BACKGROUND OF THE INVENTION  
05

06 Field of the Invention  
07

08 This invention relates to novel nitro and amino aromatic  
09 compounds. More particularly, this invention relates to  
10 novel polyalkyl nitro and amino aromatic esters and their  
11 use in fuel compositions to prevent and control engine  
12 deposits.  
13

14 Description of the Related Art  
15

16 It is well known that automobile engines tend to form  
17 deposits on the surface of engine components, such as  
18 carburetor ports, throttle bodies, fuel injectors, intake  
19 ports and intake valves, due to the oxidation and  
20 polymerization of hydrocarbon fuel. These deposits, even  
21 when present in relatively minor amounts, often cause  
22 noticeable driveability problems, such as stalling and poor  
23 acceleration. Moreover, engine deposits can significantly  
24 increase an automobile's fuel consumption and production of  
25 exhaust pollutants. Therefore, the development of effective  
26 fuel detergents or "deposit control" additives to prevent or  
27 control such deposits is of considerable importance and  
28 numerous such materials are known in the art.  
29

30 For example, aliphatic hydrocarbon-substituted phenols are  
31 known to reduce engine deposits when used in fuel  
32 compositions. U.S. Patent No. 3,849,085, issued  
33 November 19, 1974 to Kreuz et al., discloses a motor fuel  
34 composition comprising a mixture of hydrocarbons in the

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01 gasoline boiling range containing about 0.01 to 0.25 volume  
02 percent of a high molecular weight aliphatic  
03 hydrocarbon-substituted phenol in which the aliphatic  
04 hydrocarbon radical has an average molecular weight in the  
05 range of about 500 to 3,500. This patent teaches that  
06 gasoline compositions containing minor amounts of an  
07 aliphatic hydrocarbon-substituted phenol not only prevent or  
08 inhibit the formation of intake valve and port deposits in a  
09 gasoline engine, but also enhance the performance of the  
10 fuel composition in engines designed to operate at higher  
11 operating temperatures with a minimum of decomposition and  
12 deposit formation in the manifold of the engine.  
13

14 Similarly, U.S. Patent No. 4,134,846, issued January 16,  
15 1979 to Machleder et al., discloses a fuel additive  
16 composition comprising a mixture of (1) the reaction product  
17 of an aliphatic hydrocarbon-substituted phenol,  
18 epichlorohydrin and a primary or secondary mono- or  
19 polyamine, and (2) a polyalkylene phenol. This patent  
20 teaches that such compositions show excellent carburetor,  
21 induction system and combustion chamber detergency and, in  
22 addition, provide effective rust inhibition when used in  
23 hydrocarbon fuels at low concentrations.  
24

25 Amino phenols are also known to function as  
26 detergents/dispersants, antioxidants and anti-corrosion  
27 agents when used in fuel compositions. U.S. Patent  
28 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for  
29 example, discloses amino phenols having at least one  
30 substantially saturated hydrocarbon-based substituent of at  
31 least 30 carbon atoms. The amino phenols of this patent are  
32 taught to impart useful and desirable properties to  
33 oil-based lubricants and normally liquid fuels. Similar  
34

-3-

01 amino phenols are disclosed in related U.S. Patent  
02 No. 4,320,020, issued March 16, 1982 to R. M. Lange.  
03

04 Similarly, U.S. Patent No. 3,149,933, issued September 22,  
05 1964 to K. Ley et al., discloses hydrocarbon-substituted  
06 amino phenols as stabilizers for liquid fuels.  
07

08 U.S. Patent No. 4,386,939, issued June 7, 1983 to  
09 R. M. Lange, discloses nitrogen-containing compositions  
10 prepared by reacting an amino phenol with at least one 3- or  
11 4-membered ring heterocyclic compound in which the hetero  
12 atom is a single oxygen, sulfur or nitrogen atom, such as  
13 ethylene oxide. The nitrogen-containing compositions of  
14 this patent are taught to be useful as additives for  
15 lubricants and fuels.  
16

17 Nitro phenols have also been employed as fuel additives.  
18 For example, U.S. Patent No. 4,347,148, issued August 31,  
19 1982 to K. E. Davis, discloses nitro phenols containing at  
20 least one aliphatic substituent having at least about 40  
21 carbon atoms. The nitro phenols of this patent are taught  
22 to be useful as detergents, dispersants, antioxidants and  
23 demulsifiers for lubricating oil and fuel compositions.  
24

25 Similarly, U.S. Patent No. 3,434,814, issued March 25, 1969  
26 to M. Dubeck et al., discloses a liquid hydrocarbon fuel  
27 composition containing a major quantity of a liquid  
28 hydrocarbon of the gasoline boiling range and a minor amount  
29 sufficient to reduce exhaust emissions and engine deposits  
30 of an aromatic nitro compound having an alkyl, aryl,  
31 aralkyl, alkanoyloxy, alkoxy, hydroxy or halogen  
32 substituent.  
33  
34

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01 More recently, certain poly(oxyalkylene) esters have been  
02 shown to reduce engine deposits when used in fuel  
03 compositions. U.S. Patent No. 5,211,721, issued May 18,  
04 1993 to R. L. Sung et al., for example, discloses an oil  
05 soluble polyether additive comprising the reaction product  
06 of a polyether polyol with an acid represented by the  
07 formula  $\text{RCOOH}$  in which R is a hydrocarbyl radical having  
08 6 to 27 carbon atoms. The poly(oxyalkylene) ester compounds  
09 of this patent are taught to be useful for inhibiting  
10 carbonaceous deposit formation, motor fuel hazing, and as  
11 ORI inhibitors when employed as soluble additives in motor  
12 fuel compositions.

13  
14 Poly(oxyalkylene) esters of amino- and nitrobenzoic acids  
15 are also known in the art. For example, U.S. Patent  
16 No. 2,714,607, issued August 2, 1955 to M. Matter, discloses  
17 polyethoxy esters of aminobenzoic acids, nitrobenzoic acids  
18 and other isocyclic acids. These polyethoxy esters are  
19 taught to have excellent pharmacological properties and to  
20 be useful as anesthetics, spasmolytics, analeptics and  
21 bacteriostatics.

22  
23 Similarly, U.S. Patent No. 5,090,914, issued February 25,  
24 1992 to D. T. Reardan et al., discloses poly(oxyalkylene)  
25 aromatic compounds having an amino or hydrazinocarbonyl  
26 substituent on the aromatic moiety and an ester, amide,  
27 carbamate, urea or ether linking group between the aromatic  
28 moiety and the poly(oxyalkylene) moiety. These compounds  
29 are taught to be useful for modifying macromolecular species  
30 such as proteins and enzymes.

31  
32 U.S. Patent No. 4,328,322, issued September 22, 1980 to  
33 R. C. Baron, discloses amino- and nitrobenzoate esters of  
34 oligomeric polyols, such as poly(ethylene) glycol. These

01 materials are used in the production of synthetic polymers  
02 by reaction with a polyisocyanate.

03

04 In addition, U.S. Patent No. 4,231,759, issued November 4,  
05 1980 to Udelhofen et al., discloses a fuel additive  
06 composition comprising the Mannich condensation product of  
07 (1) a high molecular weight alkyl-substituted  
08 hydroxyaromatic compound wherein the alkyl group has a  
09 number average molecular weight of about 600 to about 3,000,  
10 (2) an amine, and (3) an aldehyde. This patent teaches that  
11 such Mannich condensation products provide carburetor  
12 cleanliness when employed alone, and intake valve  
13 cleanliness when employed in combination with a hydrocarbon  
14 carrier fluid.

15

16 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz  
17 et al., discloses fuel compositions containing (1) one or  
18 more polybutyl or polyisobutyl alcohols wherein the  
19 polybutyl or polyisobutyl group has a number average  
20 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)  
21 of the polybutyl or polyisobutyl alcohol, or (3) a  
22 carboxylate ester of the polybutyl or polyisobutyl alcohol.  
23 This patent further teaches that when the fuel composition  
24 contains an ester of a polybutyl or polyisobutyl alcohol,  
25 the ester-forming acid group may be derived from saturated  
26 or unsaturated, aliphatic or aromatic, acyclic or cyclic  
27 mono- or polycarboxylic acids.

28

29 U.S. Patent No. 3,285,855, issued November 15, 1966 to  
30 Dexter et al., discloses alkyl esters of dialkyl  
31 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the  
32 ester moiety contains from 6 to 30 carbon atoms. This  
33 patent teaches that such esters are useful for stabilizing  
34 polypropylene and other organic material normally subject to

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01 oxidative deterioration. Similar alkyl esters containing  
02 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.  
03 Patent No. 5,196,565, which issued March 23, 1993 to Ross.

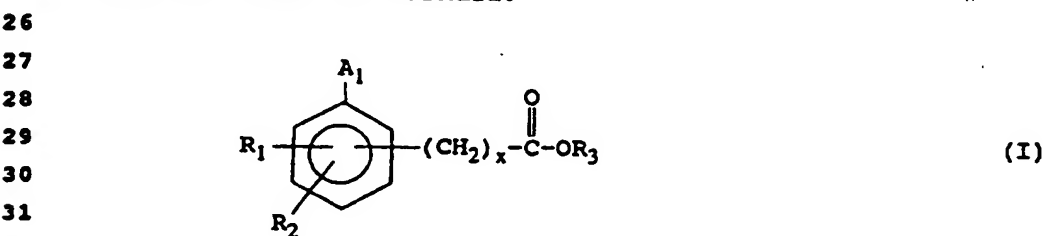
04  
05 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet  
06 et al., discloses alkyl esters of hydroxyphenyl carboxylic  
07 acids wherein the ester moiety may contain up to 23 carbon  
08 atoms. This patent teaches that such compounds are useful  
09 as antioxidants for stabilizing emulsion-polymerized  
10 polymers.

11  
12 It has now been discovered that certain polyalkyl nitro and  
13 amino aromatic esters provide excellent control of engine  
14 deposits, especially intake valve deposits, when employed as  
15 fuel additives in fuel compositions.

16  
17 SUMMARY OF THE INVENTION

18  
19 The present invention provides novel polyalkyl nitro and  
20 amino aromatic esters which are useful as fuel additives for  
21 the prevention and control of engine deposits, particularly  
22 intake valve deposits.

23  
24 The polyalkyl nitro and amino aromatic esters of the present  
25 invention have the formula:





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01 wherein A<sub>1</sub> is nitro, amino, N-alkylamino wherein the alkyl  
02 group contains 1 to 6 carbon atoms, or N,N-dialkylamino  
03 wherein each alkyl group independently contains 1 to 6  
04 carbon atoms; R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen,  
05 hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower  
06 alkoxy having 1 to 6 carbon atoms; R<sub>3</sub> is a polyalkyl group  
07 having a weight average molecular weight in the range of  
08 about 450 to 5,000; and x is an integer from 0 to 10.  
09

10 The present invention further provides a fuel composition  
11 comprising a major amount of hydrocarbons boiling in the  
12 gasoline or diesel range and an effective  
13 deposit-controlling amount of a polyalkyl nitro or amino  
14 aromatic ester of the present invention.  
15

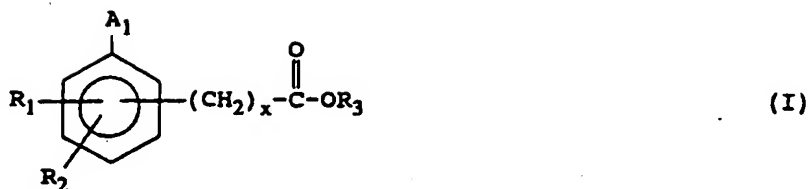
16 The present invention additionally provides a fuel  
17 concentrate comprising an inert stable oleophilic organic  
18 solvent boiling in the range of from about 150°F to 400°F  
19 and from about 10 to 70 weight percent of a polyalkyl nitro  
20 or amino aromatic ester of the present invention.  
21

22 Among other factors, the present invention is based on the  
23 surprising discovery that certain polyalkyl nitro and amino  
24 aromatic esters provide excellent control of engine  
25 deposits, especially on intake valves, when employed as fuel  
26 additives in fuel compositions.  
27

28 DETAILED DESCRIPTION OF THE INVENTION  
29

30 The fuel additives provided by the present invention have  
31 the general formula:  
32  
33  
34

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wherein A<sub>1</sub>, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and x are as defined hereinabove.

In formula I, A<sub>1</sub> is preferably a nitro, amino, or N-alkylamino group. More preferably, A<sub>1</sub> is a nitro or amino group. Most preferably, A<sub>1</sub> is an amino group.

Preferably, R<sub>1</sub> is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms. More preferably, R<sub>1</sub> is hydrogen or hydroxy. Most preferably, R<sub>1</sub> is hydroxy.

R<sub>2</sub> is preferably hydrogen.

Preferably, R<sub>3</sub> is a polyalkyl group having a weight average molecular weight in the range of about 500 to 5,000, more preferably about 500 to 3,000, and most preferably about 600 to 2,000.

Preferably, x is an integer from 0 to 2. More preferably, x is 0.

A preferred group of polyalkyl aromatic esters are those of formula I wherein R<sub>1</sub> is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R<sub>2</sub> is hydrogen; and x is 0.

Another preferred group of polyalkyl aromatic esters are those of formula I wherein R<sub>1</sub> is hydrogen, hydroxy, or lower

01 alkyl having 1 to 4 carbon atoms;  $R_2$  is hydrogen; and  $x$  is 1  
02 or 2.

03

04 A more preferred group of polyalkyl aromatic esters are  
05 those of formula I wherein  $R_1$  is hydrogen or hydroxy;  $R_2$  is  
06 hydrogen; and  $x$  is 0.

07

08 A particularly preferred group of polyalkyl aromatic esters  
09 are those wherein  $R_1$  is hydroxy,  $R_2$  is hydrogen, and  $x$  is 0.

10

11 When  $A_1$  is an *N*-alkylamino group, the alkyl group of the  
12 *N*-alkylamino moiety preferably contains 1 to 4 carbon atoms.  
13 More preferably, the alkyl group is methyl or ethyl. For  
14 example, particularly preferred *N*-alkylamino groups are  
15 *N*-methylamino and *N*-ethylamino groups.

16

17 Similarly, when  $A_1$  is an *N,N*-dialkylamino group, each alkyl  
18 group of the *N,N*-dialkylamino moiety preferably contains 1  
19 to 4 carbon atoms. More preferably, each alkyl group is  
20 either methyl or ethyl. For example, particularly preferred  
21 *N,N*-dialkylamino groups are *N,N*-dimethylamino,  
22 *N*-ethyl-*N*-methylamino and *N,N*-diethylamino groups.

23

24 A further preferred group of polyalkyl aromatic esters are  
25 those wherein  $A_1$  is amino or nitro,  $R_1$  is hydrogen or  
26 hydroxy,  $R_2$  is hydrogen, and  $x$  is 0, 1 or 2. A more  
27 preferred group of polyalkyl aromatic esters are those  
28 wherein  $A_1$  is amino or nitro,  $R_1$  is hydrogen or hydroxy,  $R_2$   
29 is hydrogen, and  $x$  is 0. A particularly preferred group of  
30 polyalkyl aromatic esters are those wherein  $A_1$  is amino or  
31 nitro,  $R_1$  is hydroxy,  $R_2$  is hydrogen, and  $x$  is 0.

32

33

34

-10-

01 It is especially preferred that the nitro, amino,  
02 *N*-alkylamino or *N,N*-dialkylamino substituent present in the  
03 aromatic moiety of the polyalkyl aromatic esters of this  
04 invention be situated in a *meta* or *para* position relative to  
05 the polyalkyl ester moiety. When the aromatic moiety also  
06 contains a hydroxyl substituent, it is particularly  
07 preferred that this hydroxyl group be in a *meta* or *para*  
08 position relative to the polyalkyl ester moiety and in an  
09 *ortho* position relative to the nitro, amino, *N*-alkylamino or  
10 *N,N*-dialkylamino substituent.

11  
12 The polyalkyl aromatic esters of the present invention will  
13 generally have a sufficient molecular weight so as to be  
14 non-volatile at normal engine intake valve operating  
15 temperatures (about 200-250°C). Typically, the molecular  
16 weight of the polyalkyl hydroxyaromatic esters of this  
17 invention will range from about 600 to about 6,000,  
18 preferably from 600 to 3,000, more preferably from 700 to  
19 2,000.

20  
21 Fuel-soluble salts of the polyalkyl aromatic esters of the  
22 present invention can be readily prepared for those  
23 compounds containing an amino, *N*-alkylamino or  
24 *N,N*-dialkylamino group and such salts are contemplated to be  
25 useful for preventing or controlling engine deposits.  
26 Suitable salts include, for example, those obtained by  
27 protonating the amino moiety with a strong organic acid,  
28 such as an alkyl- or arylsulfonic acid. Preferred salts are  
29 derived from toluenesulfonic acid and methanesulfonic acid.

30  
31 Definitions

32  
33 As used herein, the following terms have the following  
34 meanings unless expressly stated to the contrary.

-11-

01 The term "amino" refers to the group:  $\text{-NH}_2$ .

02

03 The term "N-alkylamino" refers to the group:  $\text{-NHR}_a$  wherein  
04  $R_a$  is an alkyl group. The term "N,N-dialkylamino" refers to  
05 the group:  $\text{-NR}_b\text{R}_c$ , wherein  $R_b$  and  $R_c$  are alkyl groups.

06

07 The term "alkyl" refers to both straight- and branched-chain  
08 alkyl groups.

09

10 The term "lower alkyl" refers to alkyl groups having 1 to  
11 about 6 carbon atoms and includes primary, secondary and  
12 tertiary alkyl groups. Typical lower alkyl groups include,  
13 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,  
14 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

15

16 The term "lower alkoxy" refers to the group  $\text{-OR}_d$  wherein  $R_d$   
17 is lower alkyl. Typical lower alkoxy groups include  
18 methoxy, ethoxy, and the like.

19

20 The term "polyalkyl" refers to alkyl groups which are  
21 generally derived from polyolefins which are polymers or  
22 copolymers of mono-olefins, particularly 1-mono-olefins,  
23 such as ethylene, propylene, butylene, and the like.  
24 Preferably, the mono-olefin employed will have 2 to about  
25 24 carbon atoms, and more preferably, about 3 to 12 carbon  
26 atoms. More preferred mono-olefins include propylene,  
27 butylene, particularly isobutylene, 1-octene and 1-decene.  
28 Polyolefins prepared from such mono-olefins include  
29 polypropylene, polybutene, especially polyisobutene, and the  
30 polyalphaolefins produced from 1-octene and 1-decene.

31

32

33

34

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01 General Synthetic Procedures

02

03 The polyalkyl nitro and amino aromatic esters of this  
04 invention may be prepared by the following general methods  
05 and procedures. It should be appreciated that where typical  
06 or preferred process conditions (e.g., reaction  
07 temperatures, times, mole ratios of reactants, solvents,  
08 pressures, etc.) are given, other process conditions may  
09 also be used unless otherwise stated. Optimum reaction  
10 conditions may vary with the particular reactants or  
11 solvents used, but such conditions can be determined by one  
12 skilled in the art by routine optimization procedures.

13

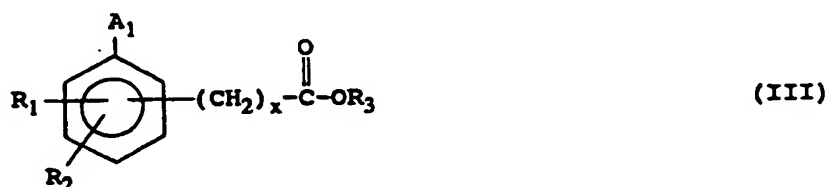
14 Moreover, those skilled in the art will recognize that it  
15 may be necessary to block or protect certain functional  
16 groups while conducting the following synthetic procedures.  
17 In such cases, the protecting group will serve to protect  
18 the functional group from undesired reactions or to block  
19 its undesired reaction with other functional groups or with  
20 the reagents used to carry out the desired chemical  
21 transformations. The proper choice of a protecting group  
22 for a particular functional group will be readily apparent  
23 to one skilled in the art. Various protecting groups and  
24 their introduction and removal are described, for example,  
25 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*  
26 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,  
27 and references cited therein.

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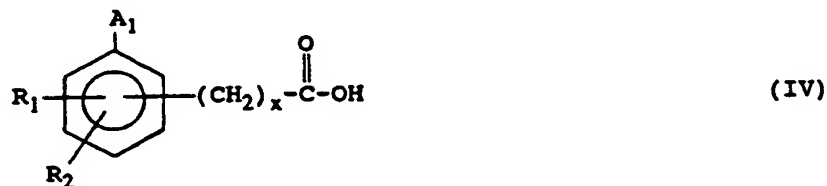
29 In the present synthetic procedures, a hydroxyl group will  
30 preferably be protected, when necessary, as the benzyl or  
31 *tert*-butyldimethylsilyl ether. Introduction and removal of  
32 these protecting groups is well described in the art. Amino  
33 groups may also require protection and this may be  
34 accomplished by employing a standard amino protecting group,

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01 such as a benzyloxycarbonyl or a trifluoroacetyl group.  
02 Additionally, as will be discussed in further detail  
03 hereinbelow, the polyalkyl aromatic esters of this invention  
04 having an amino group on the aromatic moiety will generally  
05 be prepared from the corresponding nitro derivative.  
06 Accordingly, in many of the following procedures, a nitro  
07 group will serve as a protecting group for the amino moiety.  
08  
09 The polyalkyl aromatic esters of the present invention  
10 having the formula:



wherein  $A_1$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and  $x$  are as defined above, may be prepared by esterifying an aromatic carboxylic acid having the formula:



wherein  $A_1$ ,  $R_1$ ,  $R_2$ , and  $x$  are as defined above, with a polyalkyl alcohol having the formula:



-14-

01 wherein R<sub>3</sub> is as defined above, using conventional  
02 esterification reaction conditions.

03

04 The aromatic carboxylic acids of formula IV are either known  
05 compounds or can be prepared from known compounds by  
06 conventional procedures. Representative aromatic carboxylic  
07 acids suitable for use as starting materials include, for  
08 example, 2-aminobenzoic acid (anthranilic acid),  
09 3-aminobenzoic acid, 4-aminobenzoic acid,  
10 3-amino-4-hydroxybenzoic acid, 4-amino-3-hydroxybenzoic  
11 acid, 3-aminophenylacetic acid, 4-aminophenylacetic acid,  
12 3-amino-4-methoxybenzoic acid, 4-amino-3-methoxybenzoic  
13 acid, 4-amino-3-methylbenzoic acid,  
14 4-amino-3,5-di-*t*-butylbenzoic acid, 2-nitrobenzoic acid,  
15 3-nitrobenzoic acid, 4-nitrobenzoic acid,  
16 2-nitrophenylacetic acid, 3-nitrophenylacetic acid,  
17 4-nitrophenylacetic acid, 3-hydroxy-4-nitrobenzoic acid,  
18 4-hydroxy-3-nitrobenzoic acid, 4-hydroxy-3-nitrophenylacetic  
19 acid, 3-(*N*-methylamino)benzoic acid,  
20 4-(*N*-methylamino)benzoic acid, 3-(*N*-ethylamino)benzoic acid,  
21 4-(*N*-ethylamino)benzoic acid, 3-(*N,N*-dimethylamino)benzoic  
22 acid, 4-(*N,N*-dimethylamino)benzoic acid, and the like.

23

24 Preferred aromatic carboxylic acids include 3-aminobenzoic  
25 acid, 4-aminobenzoic acid, 3-amino-4-hydroxybenzoic acid,  
26 4-amino-3-hydroxybenzoic acid, 3-nitrobenzoic acid,  
27 4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic and  
28 4-hydroxy-3-nitrobenzoic acid.

29

30 The polyalkyl alcohols of formula V may also be prepared by  
31 conventional procedures known in the art. Such procedures  
32 are taught, for example, in U.S. Patent Nos. 5,055,607 to  
33

34



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01 Buckley and 4,859,210 to Franz et al., the disclosures of  
02 which are incorporated herein by reference.

03

04 In general, the polyalkyl substituent on the polyalkyl  
05 alcohols of Formula V and the resulting polyalkyl aromatic  
06 esters of the present invention will have a weight average  
07 molecular weight in the range of about 450 to 5,000,  
08 preferably about 500 to 5,000, more preferably about 500 to  
09 3,000, and most preferably about 600 to 2,000.

10

11 The polyalkyl substituent on the polyalkyl alcohols employed  
12 in the invention may be generally derived from polyolefins  
13 which are polymers or copolymers of mono-olefins,  
14 particularly 1-mono-olefins, such as ethylene, propylene,  
15 butylene, and the like. Preferably, the mono-olefin  
16 employed will have 2 to about 24 carbon atoms, and more  
17 preferably, about 3 to 12 carbon atoms. More preferred  
18 mono-olefins include propylene, butylene, particularly  
19 isobutylene, 1-octene and 1-decene. Polyolefins prepared  
20 from such mono-olefins include polypropylene, polybutene,  
21 especially polyisobutene, and the polyalphaolefins produced  
22 from 1-octene and 1-decene.

23

24 The preferred polyisobutenes used to prepare the presently  
25 employed polyalkyl alcohols are polyisobutenes which  
26 comprise at least about 20% of the more reactive  
27 methylvinylidene isomer, preferably at least 50% and more  
28 preferably at least 70%. Suitable polyisobutenes include  
29 those prepared using  $\text{BF}_3$  catalysts. The preparation of such  
30 polyisobutenes in which the methylvinylidene isomer  
31 comprises a high percentage of the total composition is  
32 described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such  
33 polyisobutenes, known as "reactive" polyisobutenes, yield  
34

-16-

01 high molecular weight alcohols in which the hydroxyl group  
02 is at or near the end of the hydrocarbon chain.

03

04 Examples of suitable polyisobutenes having a high  
05 alkylvinylidene content include Ultravis 30, a polyisobutene  
06 having a molecular weight of about 1300 and a  
07 methylvinylidene content of about 74%, and Ultravis 10, a  
08 polyisobutene having a molecular weight of about 950 and a  
09 methylvinylidene content of about 76%, both available from  
10 British Petroleum.

11

12 The polyalkyl alcohols may be prepared from the  
13 corresponding olefins by conventional procedures. Such  
14 procedures include hydration of the double bond to give an  
15 alcohol. Suitable procedures for preparing such long-chain  
16 alcohols are described in I. T. Harrison and S. Harrison,  
17 *Compendium of Organic Synthetic Methods*, Wiley-Interscience,  
18 New York (1971), pp. 119-122, as well as in U.S. Patent  
19 Nos. 5,055,607 and 4,859,210.

20

21 As indicated above, the polyalkyl aromatic esters of formula  
22 III may be prepared by esterifying an aromatic carboxylic  
23 acid of formula IV with a polyalkyl alcohol of formula V  
24 under conventional esterification reaction conditions.

25

26 Typically, this reaction will be conducted by contacting a  
27 polyalkyl alcohol of formula V with about 0.25 to about 1.5  
28 molar equivalents of an aromatic carboxylic acid of formula  
29 IV in the presence of an acidic catalyst at a temperature in  
30 the range of about 70°C to about 160°C for about 0.5 to  
31 about 48 hours. Suitable acid catalysts for this reaction  
32 include p-toluene sulfonic acid, methanesulfonic acid and  
33 the like. The reaction may be conducted in the presence or  
34 absence of an inert solvent, such as benzene, toluene and

-17-

01 the like. The water generated by this reaction is  
02 preferably removed during the course of the reaction by, for  
03 example, azeotropic distillation with an inert solvent, such  
04 as toluene.

05

06 Alternatively, the polyalkyl aromatic esters of formula III  
07 may be prepared by reacting a polyalkyl alcohol of formula V  
08 with an acid halide derived from an aromatic carboxylic acid  
09 of formula IV, such as an acid chloride or acid bromide.

10

11 Generally, the carboxylic acid moiety of formula IV may be  
12 converted into an acyl halide moiety by contacting a  
13 compound of formula IV with an inorganic acid halide, such  
14 as thionyl chloride, phosphorous trichloride, phosphorous  
15 tribromide, or phosphorous pentachloride; or with oxalyl  
16 chloride. Typically, this reaction will be conducted using  
17 about 1 to 5 molar equivalents of the inorganic acid halide  
18 or oxalyl chloride, either neat or in an inert solvent, such  
19 as diethyl ether, at a temperature in the range of about  
20 20°C to about 80°C for about 1 to about 48 hours. A  
21 catalyst, such as *N,N*-dimethylformamide, may also be used in  
22 this reaction.

23

24 Reaction of the acid halide derived from formula IV with a  
25 polyalkyl alcohol of formula V provides a polyalkyl aromatic  
26 ester of formula III. Typically, this reaction is conducted  
27 by contacting formula V with about 0.9 to about 1.5 molar  
28 equivalents of the acid halide in an inert solvent, such as  
29 toluene, dichloromethane, diethyl ether, and the like, at a  
30 temperature in the range of about 25°C to about 150°C. The  
31 reaction is generally complete in about 0.5 to about  
32 48 hours. Preferably, the reaction is conducted in the  
33 presence of a sufficient amount of an amine capable of  
34 neutralizing the acid generated during the reaction, such as

-18-

01 triethylamine, di(isopropyl)ethylamine, pyridine or  
02 4-dimethylaminopyridine.

03

04 When the aromatic carboxylic acid of formula IV contains a  
05 hydroxyl group, for example, when R<sub>1</sub> or R<sub>2</sub> is hydroxyl,  
06 protection of the aromatic hydroxyl groups may be  
07 accomplished using well-known procedures. The choice of a  
08 suitable protecting group for a particular hydroxyaromatic  
09 carboxylic acid will be apparent to those skilled in the  
10 art. Various protecting groups, and their introduction and  
11 removal, are described, for example, in T. W. Greene and  
12 P. G. M. Wuts, *Protective Groups in Organic Synthesis*,  
13 Second Edition, Wiley, New York, 1991, and references cited  
14 therein.

15

16 Deprotection of the aromatic hydroxyl group(s) can also be  
17 accomplished using conventional procedures. Appropriate  
18 conditions for this deprotection step will depend upon the  
19 protecting group(s) utilized in the synthesis and will be  
20 readily apparent to those skilled in the art. For example,  
21 benzyl protecting groups may be removed by hydrogenolysis  
22 under 1 to about 4 atmospheres of hydrogen in the presence  
23 of a catalyst, such as palladium on carbon. Typically, this  
24 deprotection reaction is conducted in an inert solvent,  
25 preferably a mixture of ethyl acetate and acetic acid, at a  
26 temperature of from about 0°C to about 40°C for about 1 to  
27 about 24 hours.

28

29 When synthesizing the polyalkyl aromatic esters of formula I  
30 having an amino group on the aromatic moiety (i.e., where A<sub>1</sub>  
31 is an amino group), it is generally desirable to first  
32 prepare the corresponding nitro compound (i.e., where A<sub>1</sub> is  
33 a nitro group) using the above-described synthetic  
34

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01 procedures, and then to reduce the nitro group to an amino  
02 group using conventional procedures. Aromatic nitro groups  
03 may be reduced to amino groups using a number of procedures  
04 that are well known in the art. For example, aromatic nitro  
05 groups may be reduced under catalytic hydrogenation  
06 conditions; or by using a reducing metal, such as zinc, tin,  
07 iron and the like, in the presence of an acid, such as  
08 dilute hydrochloric acid.

09  
10 Generally, reduction of the nitro group by catalytic  
11 hydrogenation is preferred. Typically, this reaction is  
12 conducted using about 1 to 4 atmospheres of hydrogen and a  
13 platinum or palladium catalyst, such as palladium on carbon.  
14 The reaction is typically carried out at a temperature of  
15 about 0°C to about 100°C for about 1 to 24 hours in an inert  
16 solvent, such as ethanol, ethyl acetate and the like.  
17 Hydrogenation of aromatic nitro groups is discussed in  
18 further detail in, for example, P. N. Rylander, *Catalytic*  
19 *Hydrogenation in Organic Synthesis*, pp. 113-137, Academic  
20 Press (1979); and *Organic Synthesis, Collective Vol. I*,  
21 Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941);  
22 and references cited therein.

23

#### 24 Fuel Compositions

25

26 The polyalkyl aromatic esters of the present invention are  
27 useful as additives in hydrocarbon fuels to prevent and  
28 control engine deposits, particularly intake valve deposits.  
29 The proper concentration of additive necessary to achieve  
30 the desired deposit control varies depending upon the type  
31 of fuel employed, the type of engine, and the presence of  
32 other fuel additives.

33

34

-20-

01 In general, the concentration of the polyalkyl aromatic  
02 esters of this invention in hydrocarbon fuel will range from  
03 about 50 to about 2500 parts per million (ppm) by weight,  
04 preferably from 75 to 1,000 ppm. When other deposit control  
05 additives are present, a lesser amount of the present  
06 additive may be used.

07  
08 The polyalkyl aromatic esters of the present invention may  
09 be formulated as a concentrate using an inert stable  
10 oleophilic (i.e., dissolves in gasoline) organic solvent  
11 boiling in the range of about 150°F to 400°F (about 65°C to  
12 205°C). Preferably, an aliphatic or an aromatic hydrocarbon  
13 solvent is used, such as benzene, toluene, xylene or higher-  
14 boiling aromatics or aromatic thinners. Aliphatic alcohols  
15 containing about 3 to 8 carbon atoms, such as isopropanol,  
16 isobutylcarbinol, n-butanol and the like, in combination  
17 with hydrocarbon solvents are also suitable for use with the  
18 present additives. In the concentrate, the amount of the  
19 additive will generally range from about 10 to about  
20 70 weight percent, preferably 10 to 50 weight percent, more  
21 preferably from 20 to 40 weight percent.

22  
23 In gasoline fuels, other fuel additives may be employed with  
24 the additives of the present invention, including, for  
25 example, oxygenates, such as t-butyl methyl ether, antiknock  
26 agents, such as methylcyclopentadienyl manganese  
27 tricarbonyl, and other dispersants/detergents, such as  
28 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or  
29 succinimides. Additionally, antioxidants, metal  
30 deactivators and demulsifiers may be present.

31  
32 In diesel fuels, other well-known additives can be employed,  
33 such as pour point depressants, flow improvers, cetane  
34 improvers, and the like.

-21-

01 A fuel-soluble, nonvolatile carrier fluid or oil may also be  
02 used with the polyalkyl aromatic esters of this invention.  
03 The carrier fluid is a chemically inert hydrocarbon-soluble  
04 liquid vehicle which substantially increases the nonvolatile  
05 residue (NVR), or solvent-free liquid fraction of the fuel  
06 additive composition while not overwhelmingly contributing  
07 to octane requirement increase. The carrier fluid may be a  
08 natural or synthetic oil, such as mineral oil, refined  
09 petroleum oils, synthetic polyalkanes and alkenes, including  
10 hydrogenated and unhydrogenated polyalphaolefins, and  
11 synthetic polyoxyalkylene-derived oils, such as those  
12 described, for example, in U.S. Patent No. 4,191,537 to  
13 Lewis, and polyesters, such as those described, for example,  
14 in U.S. Patent Nos. 3,756,793 and 5,004,478 to Robinson and  
15 Vogel et al., respectively, and in European Patent  
16 Application Nos. 356,726 and 382,159, published March 7,  
17 1990 and August 16, 1990, respectively.

18  
19 These carrier fluids are believed to act as a carrier for  
20 the fuel additives of the present invention and to assist in  
21 removing and retarding deposits. The carrier fluid may also  
22 exhibit synergistic deposit control properties when used in  
23 combination with a polyalkyl aromatic ester of this  
24 invention.

25  
26 The carrier fluids are typically employed in amounts ranging  
27 from about 100 to about 5000 ppm by weight of the  
28 hydrocarbon fuel, preferably from 400 to 3000 ppm of the  
29 fuel. Preferably, the ratio of carrier fluid to deposit  
30 control additive will range from about 0.5:1 to about 10:1,  
31 more preferably from 1:1 to 4:1, most preferably about 2:1.

32  
33 When employed in a fuel concentrate, carrier fluids will  
34 generally be present in amounts ranging from about 20 to

-22-

01 about 60 weight percent, preferably from 30 to 50 weight  
02 percent.

03

04

#### EXAMPLES

05

06 The following examples are presented to illustrate specific  
07 embodiments of the present invention and synthetic  
08 preparations thereof; and should not be interpreted as  
09 limitations upon the scope of the invention.

10

11

#### Example 1

12

13

#### Preparation of Polyisobutyl-4-Nitrobenzoate

14

15 4-Nitrobenzoyl chloride (12.7 grams) was combined with  
16 47.6 grams of polyisobutanol (molecular weight average 984,  
17 prepared via hydroformylation of Amoco H-100 polyisobutene)  
18 and 300 mL of anhydrous toluene. Triethylamine (10.0 mL)  
19 and 4-dimethylaminopyridine (4.2 grams) were then added and  
20 the resulting mixture heated to reflux under nitrogen for  
21 sixteen hours. The reaction was cooled to room temperature  
22 and diluted with diethyl ether. The organic layer was  
23 washed twice with 1% aqueous hydrochloric acid, twice with  
24 aqueous sodium bicarbonate solution, and once with brine.  
25 The organic layer was then dried over anhydrous magnesium  
26 sulfate, filtered and the solvents removed in vacuo to yield  
27 41.9 grams of a yellow oil. The oil was chromatographed on  
28 silica gel, eluting with hexane/ethylacetate/ethanol  
29 (9:0.8:0.2) to yield 37.2 grams of the desired product as a  
30 light yellow oil. IR (neat)  $1725\text{ cm}^{-1}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$   
31 8.3, 8.2 (AB quartet, 4H), 4.35 (t, 2H), 0.6-1.8 (m, 137H).

32

33

34



-23-

Example 2Preparation of Polyisobutyl-4-Aminobenzoate

A solution of 30.75 grams of the product from Example 1 in 220 mL of ethyl acetate containing 3.5 grams of 10% palladium on charcoal was hydrogenated at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yielded 29.44 grams of the desired product as a light yellow oil. IR (neat) 1709, 1696  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.9 (d, 2H), 6.65 (d, 2H), 4.3 (t, 2H), 4.1 (bs, 2H), 0.6-1.8 (m, 137H).

Example 3Preparation of Polyisobutyl-3-Nitro-4-Hydroxybenzoate

To a flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, reflux condenser and nitrogen inlet was added 35.0 grams of polyisobutanol (molecular weight average 984, prepared via hydroformylation of Amoco H-100 polyisobutene), 11.0 grams of 3-nitro-4-hydroxybenzoic acid and 0.86 grams of p-toluene sulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 500 mL of diethyl ether. The organic phase was washed twice with saturated aqueous sodium bicarbonate solution, once with brine, dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 35.0 grams of a brown oil. The oil was chromatographed on silica gel eluting with hexane/ethyl acetate/ethanol (8:1.8:0.2) to yield 25.4 grams of the desired product as a light brown oil. IR (neat) 1721  $\text{cm}^{-1}$ .

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01 <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 10.9 (s, 1H), 8.85 (s, 1H), 8.25 (d, 1H),  
02 7.2 (d, 1H), 4.35 (t, 2H), 0.6-1.8 (m, 137H).  
03

04 Example 4  
05

06 Preparation of Polyisobutyl-3-Hydroxy-4-Nitrobenzoate  
07

08 To a flask equipped with a mechanical stirrer, thermometer,  
09 Dean-Stark trap, reflux condensor and nitrogen inlet was  
10 added 35.0 grams of polyisobutanol (molecular weight average  
11 984, prepared via hydroformylation of Amoco H-100  
12 polyisobutene), 11.0 grams of 3-hydroxy-4-nitrobenzoic acid  
13 and 0.86 grams of p-toluene sulfonic acid. The mixture was  
14 stirred at 130°C for sixteen hours, cooled to room  
15 temperature and diluted with 500 mL of diethyl ether. The  
16 organic phase was washed twice with saturated aqueous sodium  
17 bicarbonate solution, once with brine, dried over anhydrous  
18 magnesium sulfate, filtered and concentrated in vacuo to  
19 yield 37.8 grams of a black oil. The oil was  
20 chromatographed on silica gel eluting with hexane/ethyl  
21 acetate/ethanol (8:1.8:0.2) to yield 27.9 grams of the  
22 desired product as a brown oil. IR (neat) 1731cm<sup>-1</sup>. <sup>1</sup>H NMR  
23 (CDCl<sub>3</sub>) δ 10.5 (s, 1H), 8.2 (d, 1H), 7.8 (s, 1H), 7.65 (d,  
24 1H), 4.35 (t, 2H), 0.6-1.8 (m, 137H).  
25

26 Example 5  
27

28 Preparation of Polyisobutyl-3-Amino-4-Hydroxybenzoate  
29

30 A solution of 19.0 grams of the product from Example 3 in  
31 200 mL of ethyl acetate containing 3.0 grams of 10%  
32 palladium on charcoal was hydrogenolyzed at 35-40 psi for  
33 sixteen hours on a Parr low-pressure hydrogenator. Catalyst  
34

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01 filtration and removal of the solvent in vacuo yielded  
02 17.4 grams of the desired product as a light brown oil. IR  
03 (neat) 1716, 1682  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.45 (m, 2H), 6.75  
04 (d, 1H), 4.3 (t, 2H), 0.6-1.8 (m, 137H).  
05

06 Example 6  
07

08 Preparation of Polyisobutyl-3-Hydroxy-4-Aminobenzoate  
09

10 A solution of 21.35 grams of the product from Example 4 in  
11 200 mL of ethyl acetate containing 3.0 grams of 10%  
12 palladium on charcoal was hydrogenolyzed at 35-40 psi for  
13 sixteen hours on a Parr low-pressure hydrogenator. Catalyst  
14 filtration and removal of the solvent in vacuo yielded  
15 20.6 grams of the desired product as a light brown oil. IR  
16 (neat) 1709, 1682  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.6 (s, 1H), 7.5  
17 (d, 1H), 6.7 (d, 1H), 4.3 (t, 2H), 0.6-1.8 (m, 137H).  
18

19 Example 7  
20

21 Single-Cylinder Engine Test  
22

23 The test compounds were blended in gasoline and their  
24 deposit reducing capacity determined in an ASTM/CFR  
25 single-cylinder engine test.  
26

27 A Waukesha CFR single-cylinder engine was used. Each run  
28 was carried out for 15 hours, at the end of which time the  
29 intake valve was removed, washed with hexane and weighed.  
30 The previously determined weight of the clean valve was  
31 subtracted from the weight of the valve at the end of the  
32 run. The differences between the two weights is the weight  
33 of the deposit. A lesser amount of deposit indicates a  
34

-26-

01 superior additive. The operating conditions of the test  
02 were as follows: water jacket temperature 200°F; vacuum of  
03 12 in Hg, air-fuel ratio of 12, ignition spark timing of  
04 40° BTC; engine speed is 1800 rpm; the crankcase oil is a  
05 commercial 30W oil.

06  
07 The amount of carbonaceous deposit in milligrams on the  
08 intake valves is reported for each of the test compounds in  
09 Table I.

TABLE I

Intake Valve Deposit Weight  
(in milligrams)

14 Sample <sup>1</sup>	Run 1	Run 2	Average
15 Base Fuel	176.4	179.2	177.8
16 Example 1	171.0	159.4	165.2
17 Example 2	10.0	16.6	13.3
18 Example 3	130.0	143.5	136.8
19 Example 4	139.0	127.0	133.0
20 Example 5	0.0	0.4	0.2
21 Example 6	0.0	0.2	0.1

22  
23  
24 <sup>1</sup>At 200 parts per million actives (ppma).

25  
26 The base fuel employed in the above single-cylinder engine  
27 tests was a regular octane unleaded gasoline containing no  
28 fuel detergent. The test compounds were admixed with the  
29 base fuel to give a concentration of 200 ppma (parts per  
30 million actives).

31  
32 The data in Table I illustrates the significant reduction in  
33 intake valve deposits provided by the polyalkyl aromatic  
34

-27-

01 esters of the present invention (Examples 1, 2, 3, 4, 5 and  
02 6) compared to the base fuel.

03

04 Example 8

05

06 Multicylinder Engine Test

07

08 The polyalkyl aromatic esters of the present invention were  
09 tested in a laboratory multicylinder engine to evaluate  
10 their intake valve and combustion chamber deposit control  
11 performance. The test engine was a 4.3 liter, TBI (throttle  
12 body injected), V6 engine manufactured by General Motors  
13 Corporation.

14

15 The major engine dimensions are set forth in Table II:

16

17

18 Table II

19

20 Engine Dimensions

21

21	Bore	10.16 cm
22	Stroke	8.84 cm
23	Displacement Volume	4.3 liter
24	Compression Ratio	9.3:1

25

26

27 The test engine was operated for 40 hours (24 hours a day)  
28 on a prescribed load and speed schedule representative of  
29 typical driving conditions. The cycle for engine operation  
30 during the test is set forth in Table III.

31

32

33

34

-28-

Table III

Engine Driving Cycle

Step	Mode	Time in Mode [Sec] <sup>1</sup>	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

<sup>1</sup> All steps, except step number 3, include a 15 second transition ramp. Step 3 includes a 20 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table IV.

-29-

Table IV  
Multicylinder Engine Test Results

Sample <sup>1</sup>		Intake Valve Deposits <sup>2</sup>	Combustion Chamber Deposits <sup>2</sup>
Base Fuel	Run 1	710	2339
	Run 2	962	2059
	Average	836	2199
Example 5	Run 1	165	2596
	Run 2	143	2566
	Average	154	2581

<sup>1</sup> At 200 parts per million actives (ppma) plus 800 ppm Chevron 500 neutral oil.

<sup>2</sup> In milligrams (mg).

The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives) plus 800 ppm of the carrier fluid Chevron 500 neutral oil.

The data in Table IV illustrates the significant reduction in intake valve deposits provided by the polyalkyl aromatic esters of the present invention (Example 5) compared to the base fuel. Moreover, the data in Table IV further demonstrates that the polyalkyl aromatic esters of the present invention do not contribute significantly to combustion chamber deposits.

-30-

01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

05

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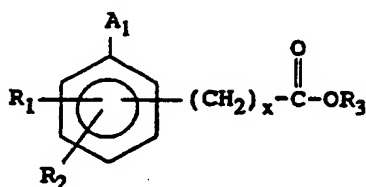
30

31

32

33

34



wherein  $A_1$  is nitro, amino, *N*-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or *N,N*-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

$R_1$  and  $R_2$  are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

$R_3$  is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and  $x$  is an integer from 0 to 10.

2. The compound according to Claim 1, wherein  $R_1$  is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms.

3. The compound according to Claim 2, wherein  $R_1$  is hydrogen or hydroxy.

4. The compound according to Claim 3, wherein  $R_1$  is hydroxy.

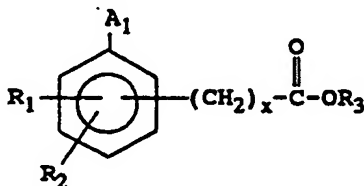


-31-

- 01 5. The compound according to Claim 1, wherein  $R_2$  is  
02 hydrogen.  
03
- 04 6. The compound according to Claim 1, wherein  $x$  is 0, 1 or  
05 2.  
06
- 07 7. The compound according to Claim 6, wherein  $R_1$  and  $R_2$   
08 are hydrogen, and  $x$  is 0.  
09
- 10 8. The compound according to Claim 6, wherein  $R_1$  is  
11 hydroxy,  $R_2$  is hydrogen, and  $x$  is 0.  
12
- 13 9. The compound according to Claim 17, wherein  $A_1$  is nitro  
14 or amino.  
15
- 16 10. The compound according to Claim 9, wherein  $A_1$  is amino.  
17
- 18 11. The compound according to Claim 1, wherein  $R_3$  is a  
19 polyalkyl group having a weight average molecular  
20 weight in the range of about 500 to 5,000.  
21
- 22 12. The compound according to Claim 11, wherein  $R_3$  has a  
23 weight average molecular weight in the range of about  
24 500 to 3,000.  
25
- 26 13. The compound according to Claim 12, wherein  $R_3$  has a  
27 weight average molecular weight in the range of about  
28 600 to 2,000.  
29
- 30 14. The compound according to Claim 1, wherein  $R_3$  is a  
31 polyalkyl group derived from polypropylene, polybutene,  
32 or polyalphaolefin oligomers of 1-octene or 1-decene.  
33  
34

-32-

- 01 15. The compound according to Claim 14, wherein  $R_3$  is  
 02 derived from polyisobutene.  
 03
- 04 16. The compound according to Claim 15, wherein the  
 05 polyisobutene contains at least about 20% of a  
 06 methylvinylidene isomer.  
 07
- 08 17. A fuel composition comprising a major amount of  
 09 hydrocarbons boiling in the gasoline or diesel range  
 10 and an effective detergent amount of a compound of the  
 11 formula:  
 12



19 wherein  $A_1$  is nitro, amino, *N*-alkylamino wherein the  
 20 alkyl group contains 1 to 6 carbon atoms, or  
 21 *N,N*-dialkylamino wherein each alkyl group independently  
 22 contains 1 to 6 carbon atoms;  
 23

24  $R_1$  and  $R_2$  are independently hydrogen, hydroxy, lower  
 25 alkyl having 1 to 6 carbon atoms, or lower alkoxy  
 26 having 1 to 6 carbon atoms;  
 27

28  $R_3$  is a polyalkyl group having a weight average  
 29 molecular weight in the range of about 450 to 5,000;  
 30 and  $x$  is an integer from 0 to 10.  
 31  
 32  
 33  
 34

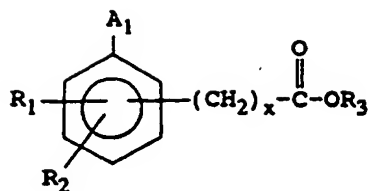
-33-

- 01 18. The fuel composition according to Claim 17, wherein  $R_1$   
02 is hydrogen, hydroxy, or lower alkyl having 1 to 4  
03 carbon atoms.  
04
- 05 19. The fuel composition according to Claim 18, wherein  $R_1$   
06 is hydrogen or hydroxy.  
07
- 08 20. The fuel composition according to Claim 19, wherein  $R_1$   
09 is hydroxy.  
10
- 11 21. The fuel composition according to Claim 1, wherein  $R_2$   
12 is hydrogen.  
13
- 14 22. The fuel composition according to Claim 17, wherein  $x$   
15 is 0, 1 or 2.  
16
- 17 23. The fuel composition according to Claim 22, wherein  $R_1$   
18 and  $R_2$  are hydrogen, and  $x$  is 0.  
19
- 20 24. The fuel composition according to Claim 22, wherein  $R_1$   
21 is hydroxy,  $R_2$  is hydrogen, and  $x$  is 0.  
22
- 23 25. The fuel composition according to Claim 17, wherein  $A_1$   
24 is nitro or amino.  
25
- 26 26. The fuel composition according to Claim 25, wherein  $A_1$   
27 is amino.  
28
- 29 27. The fuel composition according to Claim 17, wherein  $R_3$   
30 is a polyalkyl group having a weight average molecular  
31 weight in the range of about 500 to 5,000.  
32  
33  
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- 01 28. The fuel composition according to Claim 27, wherein  $R_3$   
02 has a weight average molecular weight in the range of  
03 about 500 to 3,000.  
04
- 05 29. The fuel composition according to Claim 28, wherein  $R_3$   
06 has a weight average molecular weight in the range of  
07 about 600 to 2,000.  
08
- 09 30. The fuel composition according to Claim 17, wherein  $R_3$   
10 is a polyalkyl group derived from polypropylene,  
11 polybutene, or polyalphaolefin oligomers of 1-octene or  
12 1-decene.  
13
- 14 31. The fuel composition according to Claim 30, wherein  $R_3$   
15 is derived from polyisobutene.  
16
- 17 32. The fuel composition according to Claim 31, wherein the  
18 polyisobutene contains at least about 20% of a  
19 methylvinylidene isomer.  
20
- 21 33. The fuel composition according to Claim 17, wherein  
22 said composition contains about 50 to about 2500 parts  
23 per million by weight of said compound.  
24
- 25 34. A fuel concentrate comprising an inert stable  
26 oleophilic organic solvent boiling in the range of from  
27 about 150°F to 400°F and from about 10 to about 70  
28 weight percent of a compound of the formula:  
29  
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wherein  $A_1$  is nitro, amino, *N*-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or *N,N*-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

$R_1$  and  $R_2$  are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

$R_3$  is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and  $x$  is an integer from 0 to 10.

35. The fuel concentrate according to Claim 34, wherein  $R_1$  is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms.
36. The fuel concentrate according to Claim 35, wherein  $R_1$  is hydrogen or hydroxy.
37. The fuel concentrate according to Claim 36, wherein  $R_1$  is hydroxy.
38. The fuel concentrate according to Claim 34, wherein  $R_2$  is hydrogen.

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- 01 39. The fuel concentrate according to Claim 34, wherein x  
02 is 0, 1 or 2.  
03
- 04 40. The fuel concentrate according to Claim 39, wherein R<sub>1</sub>  
05 and R<sub>2</sub> are hydrogen, and x is 0.  
06
- 07 41. The fuel concentrate according to Claim 39, wherein R<sub>1</sub>  
08 is hydroxy, R<sub>2</sub> is hydrogen, and x is 0.  
09
- 10 42. The fuel concentrate according to Claim 34, wherein A<sub>1</sub>  
11 is nitro or amino.  
12
- 13 43. The fuel concentrate according to Claim 42, wherein A<sub>1</sub>  
14 is amino.  
15
- 16 44. The fuel concentrate according to Claim 34, wherein R<sub>3</sub>  
17 is a polyalkyl group having a weight average molecular  
18 weight in the range of about 500 to 5,000.  
19
- 20 45. The fuel concentrate according to Claim 44, wherein R<sub>3</sub>  
21 has a weight average molecular weight in the range of  
22 about 500 to 3,000.  
23
- 24 46. The fuel concentrate according to Claim 45, wherein R<sub>3</sub>  
25 has a weight average molecular weight in the range of  
26 about 600 to 2,000.  
27
- 28 47. The fuel concentrate according to Claim 34, wherein R<sub>3</sub>  
29 is a polyalkyl group derived from polypropylene,  
30 polybutene, or polyalphaolefin oligomers of 1-octene or  
31 1-decene.  
32  
33  
34

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- 01 48. The fuel concentrate according to Claim 47, wherein  $R_3$   
02 is derived from polyisobutene.  
03
- 04 49. The fuel concentrate according to Claim 48, wherein the  
05 polyisobutene contains at least about 20% of a  
06 methylvinylidene isomer.  
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/13797

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/18; C07C 205/00, 229/00

US CL : 44/399, 410; 560/23, 43

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/399, 410; 560/23, 43

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS ONLINE

search terms: amino-hexyldecyl benzoic acid, nitrobenzoate, hydroxybenzoate, fuel

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 2,252,089 (Miller) 12 August 1941, col. 1, lines 1-4, 51-55; col. 2, lines 1-29.	1-49
A	US, A, 3,929,864 (Papenfuss) 30 December 1975, see entire document.	1-16
A	US, A, 4,058,550 (Shepherd et al) 15 November 1977, see entire document.	1-16
A	JP, A, 56-169650 (Nippon) 26 December 1981, see abstract.	1-16
A	JP, A, 62-016450 (Nisshin) 24 January 1987, see abstract.	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

17 JANUARY 1995

Date of mailing of the international search report

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